Copper(I)-Catalyzed Boryl Substitution of 1-Trifluoromethyl Allenes for the Synthesis of 3-Boryl-Substituted 1,1-*gem*-Difluorodienes

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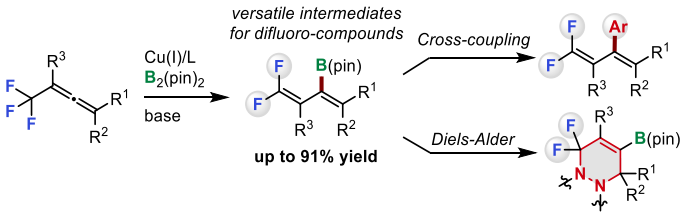
Supporting Information Placeholder



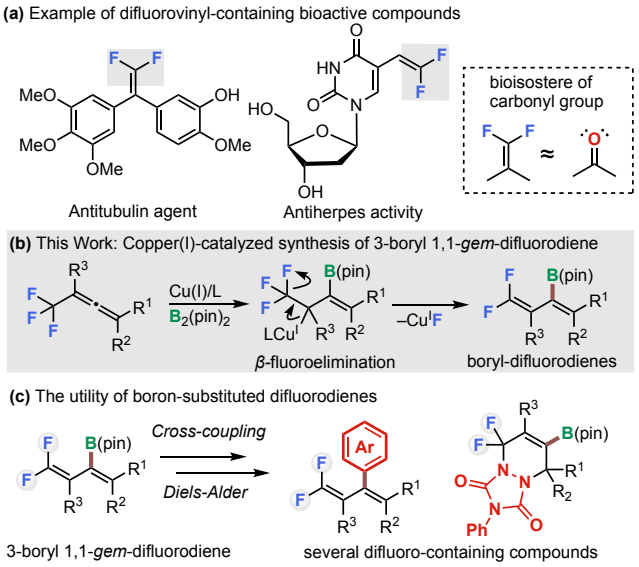
ABSTRACT: A method to synthesize 3-boryl-1,1-*gem*-difluorodienes via the copper(I)-catalyzed boryl substitution of trifluoromethyl-substituted allenes was developed. The borylated compounds were obtained in up to 91% yield with excellent selectivity. We proposed that the reaction proceeded via γ-selective borylcupration into the trifluoromethyl-substituted allene followed by copper(I)-*β*-fluoro elimination. Subsequent transformations of the borylation product by Suzuki–Miyaura cross-coupling or Diels–Alder reaction provided various compounds bearing a difluoro moiety, which are difficult to synthesize by existing methods.

INTRODUCTION

Organofluorine compounds are used in many applications in various research fields because the introduction of fluorine atom(s) or fluorinated moieties into organic molecules can dramatically alter the reactivity and physical, chemical, and biological properties of target molecules.[1] Among numerous fluorine-containing compounds, the *gem*-difluoroalkenyl moiety, which has been considered isosteric and isopolar to carbonyl groups, is an attractive target. Thus, demand for efficient methods to access compounds with a *gem*-difluoroalkenyl group has increased steadily (Scheme 1a).[2,3]

Fluorine-containing organoboron compounds are attractive synthons that have great potential for the flexible assembly of an array of structurally diverse organofluorine compounds.[2c,4] Recently, several groups have reported the selective syntheses of fluorine-containing organoboron compounds through transition metal-mediated C–F bond activation.[5,6] We previously reported the copper(I)-catalyzed enantioselective borylation reactions of allyltrifluorides and allyldifluorides using bis(pinacolato)diboron.[7] These reactions presumably proceed through the enantioselective borylcupration of alkenes, followed by copper(I)-*β*-fluoro elimination to give *gem*-difluoroallylboronates.[8,9] Based on our studies, we anticipated that 3-boryl-1,1-*gem*-difluorodienes could be efficiently synthesized by the borylation of 1-trifluoromethyl-substituted allenes through the regioselective borylcupration/copper(I)-*β*-fluoro elimination sequence (Scheme 1b).[9c,10,11] The products would be versatile intermediates to obtain potentially useful *gem*-difluoroalkenyl compounds, which are difficult to obtain by other methods, through cross-coupling reactions with aryl halides. In addition, a Diels–Alder reaction between the product and an electron-deficient alkene would allow the construction of complex structural motifs containing a difluoromethyl moiety (Scheme 1c).

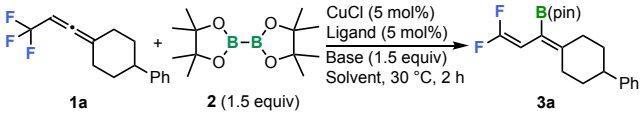
Scheme 1. The Aims of This Study



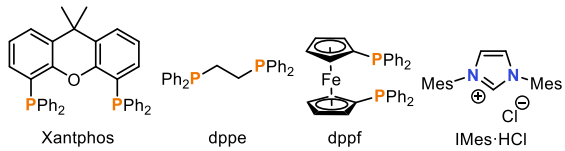
RESULT AND DISCUSSION

We began by searching for optimal conditions for the transformation of CF_3-substituted allene **1a** (Table 1). With CuCl/PPh_3 (5 mol%), $B_2(pin)_2$ (**2**), and NaOMe, **3a** was generated from **1a** in 92% yield (Table 1, entry 1). The use of other diphosphine ligands such as Xantphos, dppe, and dppf also provided **3a** in high yield (Table 1, entries 2–4). However, the use of an imidazolium salt such as 1,3-dimesitylimidazolium chloride (IMes•HCl) as a precursor of the corresponding *N*-heterocyclic carbene (NHC) ligand led to a substantial decrease in reactivity (Table 1, entry 5). The nature of the bases was also found to have a marked impact on the reactivity (Table 1, entries 6–8). For example, the use of Na(O-*t*-Bu) and K(O-*t*-Bu) resulted in a slight change in reactivity, whereas the use of other bases such as LiOMe led to a considerable decrease in reactivity. These results indicated that the choice of the counter cation of the base is crucial for this reaction. Changing the solvent from THF to 1,3-dimethyl-2-imidazolidinone (DMI) or toluene provided similar results (Table 1, entries 9 and 10). In fact, the yield is the highest with DMI solvent, but we chose THF as the solvent considering ease of handling. Use of a catalytic amount of NaOMe resulted in a low yield (27%, Table 1, entry 11). Finally, in the absence of ligand, the reaction proceeded but a decreased yield was observed (69%, Table 1, entry 12).

Table 1. Optimization of the Reaction Conditions[a]



Entry	Ligand	Base	Solvent	Yield (%)[b]
1	PPh_3	NaOMe	THF	92
2	Xantphos	NaOMe	THF	87
3	dppe	NaOMe	THF	89
4	dppf	NaOMe	THF	89
5	IMes	NaOMe	THF	trace
6	PPh_3	Na(O-*t*-Bu)	THF	92
7	PPh_3	K(O-*t*-Bu)	THF	87
8	PPh_3	LiOMe	THF	trace
9	PPh_3	NaOMe	DMI	95
10	PPh_3	NaOMe	Toluene	78
11[c]	PPh_3	NaOMe	THF	27
12	none	NaOMe	THF	69

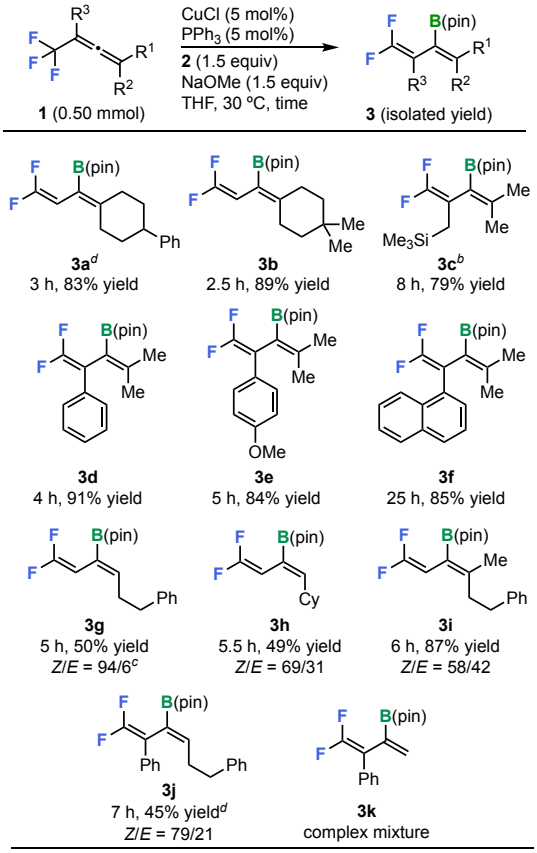


[a]Conditions: **1** (0.25 mmol), CuCl (0.0125 mmol), ligand (0.0125 mmol), base (0.375 mmol), **2** (0.375 mmol) in THF (500 μL). [b]Determined by ^{19}F NMR analysis of the crude mixture with a fluorobenzene as an internal standard. [c]NaOMe (10 mol%) was used as the base.

Next, the optimized conditions were used to evaluate the substrate scope (Table 2). Model substrate **1a** and the similar substrate **1b** were reacted with **2** under the optimized conditions to give the corresponding products in high yield (**3a:** 83%, **3b**: 89%, **3a** contained trace amounts of byproducts). Tetrasubstituted allenes bearing a silyl group (**1c**) or aryl group (**1d–1f**) also reacted smoothly to give corresponding multisubstituted *gem*-difluorodienes (**3c**: 79%, **3d**: 91%, **3e**: 84%, and **3f**: 85%). Furthermore, we conducted the reaction using trifluoromethyl allenes with asymmetric substituents on the C3 carbon atom. The reaction of a substrate with 3-monosubstituted allene **1g** proceeded smoothly with high *Z*/*E* ratio (**3g**: 50%, *Z*/*E* = 94/6).[12] Although cyclohexyl-substituted product **3h** was obtained with similar reactivity to that of the other substrates, a lower *Z*/*E* ratio was observed (**3h**: 49%, *Z*/*E* = 69/31). In addition, 3,3-disubstituted and 1,3-disubstituted trifluoromethyl allenes were converted to the corresponding products but low to moderate *Z*/*E* ratios were observed (**3i**: 87%, *Z*/*E* = 58/42; **3j**: 45%, *Z*/*E* = 79/21, **3j** contained trace amounts of byproducts). Unfortunately, the reaction

of trifluoromethyl-substituted terminal allene **1k** resulted in a complex mixture.

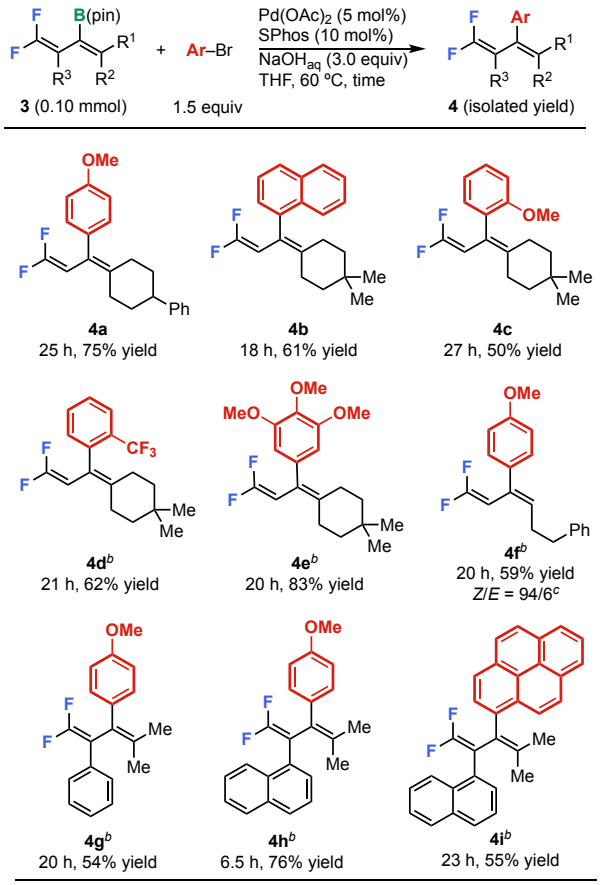
Table 2. Scope of 3-Boryl-1,1-*gem*-Difluorodiene Formation[a]



[a]Conditions: **1** (0.50 mmol), CuCl (0.025 mmol), PPh_3 (0.025 mmol), NaOMe (0.75 mmol), and **2** (0.75 mmol) in THF (1.0 mL). [b]Conducted on 0.25 mmol scale. [c]Determined by GC and 2D NOESY analyses. [d]Contained a small amount of byproduct. See the Supporting Information for details.

We conducted several transformation reactions to demonstrate the utility of the newly synthesized 3-boryl-1,1-*gem*-difluorodienes (Table 3). First, we focused on Suzuki–Miyaura cross-coupling reactions using the boryl substitution products with aryl halides as the coupling partner.[13] This transformation would provide useful routes to synthesize functionalized difluoro compounds in a stereoretentive manner. The reaction of **3a** with *p*-methoxyphenyl bromide in the presence of $Pd(OAc)_2$/SPhos as a catalyst afforded the corresponding coupling product in high yield (**4a**: 75%). The reaction of **3b** with naphthyl bromide and *o*-methoxy bromide afforded the corresponding difluoro compounds in moderate yield (**4b**: 61%, **4c**: 50%). Other aryl bromides bearing an electron-deficient CF_3 or 3,4,5-trimethoxy group were also suitable substrates for this transformation (**4d**: 62%, **4e**: 83%). Furthermore, **4f** was obtained from **3g** and retained a high *Z*/*E* ratio (**4f**: 59%, *Z*/*E* = 94/6). The reaction of **3d** and **3f** with *p*-methoxyphenyl bromide provided interesting π-conjugated difluoroalkenyl compounds **4g** and **4h**, respectively (**4g**: 54%, **4h**: 76%). In addition, π-conjugated **4i** was obtained by reaction with 1-bromopyrene. These π-conjugated difluoroalkenyl compounds are potentially useful building blocks for fluorinated organic materials but are difficult to prepare using existing methods.[14]

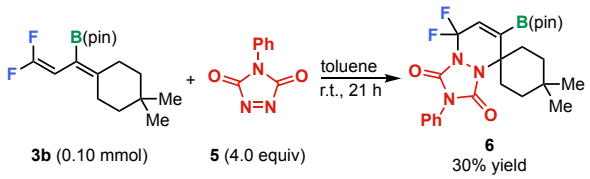
Table 3. Cross-Coupling Reactions of 3 with Aryl Bromides[a]



[a]Conditions: **3** (0.10 mmol), ArBr (0.15 mmol), $Pd(OAc)_2$ (0.005 mmol), SPhos (0.010 mmol), and 2.5M $NaOH_{aq}$ (0.30 mmol) in THF (210 μL). [b]ArBr (1.05 equiv) was used. [c]Determined by GC analysis.

Next, we conducted the Diels–Alder reaction of **3b**.[15] Although commonly used dienophiles such as maleic anhydride found to be unreactive to **3b**, the reaction of **3b** with a highly reactive dienophile **5** afforded difluoro-containing heterocyclic vinyl boronate **6** in 30% yield (Scheme 2). This derivatization provides a synthetic route to access complex fluorinated compounds.

Scheme 2. Diels–Alder Reaction of 3b with a Dienophile.



We propose a possible reaction mechanism for the current copper(I)-catalyzed borylation of trifluoromethyl-substituted allenes, which is shown in Figure 1a.[7,9c] The reaction of CuCl with the ligand and NaOMe would result in the formation of copper(I) alkoxide intermediate **A**, which would initially react with diboron **2** to afford the boryl copper(I) intermediate **B**. Then, the C–C double bond of an allene inserts into the Cu–B bond of intermediate **B** to afford σ-allyl copper intermediates **C** and **D.** Subsequent *β*-fluoro elimination of **C** gives 3-boryl *gem*-difluorodiene **3** and a copper(I) fluoride intermediate **E,** which would react with NaOMe to regenerate copper(I) alkoxide intermediate **A** and close the catalytic cycle. The variations in the *Z*/*E* ratios of substrates **3g**–**3j** may be caused by the fast η^1–η^3 interconversion from **C** to **D**, in which the equilibrium between **C** and **D** depends on the substituents on the allene (Figure 1b). The proposed reason for the complex mixture obtained from the reaction of substrate **3k** would be the difficulty of *β*-fluoro elimination because the less sterically hindered intermediate **D** is more stable than **C**, which traps the reaction.

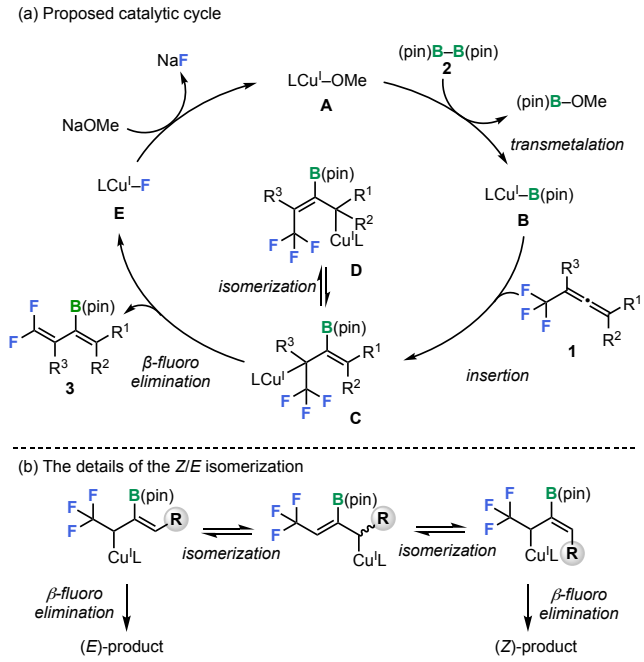


Figure 1. Proposed reaction mechanism for the copper(I)-catalyzed borylation of trifluoromethyl allenes.

In conclusion, we developed a copper(I)-catalyzed boryl substitution reaction of trifluoromethyl-substituted allenes that provides access to novel difluoro compounds. The cross-coupling reactions between the borylation products and aryl bromides provided functionalized difluorodiene derivatives in good yield. Additionally, we obtained a difluoro-containing cyclic vinyl boronate through a Diels–Alder reaction. We believe that the newly synthesized organoboron reagents—3-boryl-1,1-*gem*-difluorodienes—which are difficult to access by previous synthetic methods, will be useful building blocks for the preparation of various organofluorine compounds.

EXPERIMENTAL SECTION

General. Materials were obtained from commercial suppliers and purified by standard procedures unless otherwise noted. Solvents were also purchased from commercial suppliers, degassed via three freeze-pump-thaw cycles, and further dried over molecular sieves (MS 4A). NMR spectra were recorded on JEOL JNM-ECX400P and JNM-ECS400 spectrometers (^{1}H: 392, 396, 400 and 401 MHz, ^{13}C: 99 and 100 MHz and ^{19}F: 373 MHz). Tetramethylsilane (^{1}H), $CDCl_3$ (^{13}C) and fluorobenzene (^{19}F, δ –113.60) were employed as the external standards, respectively. Fluorobenzene was used as an internal standard to determine NMR yield. ^{13}C NMR peak assignments of all compounds were confirmed by DEPT analysis. Multiplicity was recorded as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. CuCl (ReagentPlus® grade, 224332-25G, ≥99%) were purchased from Sigma-Aldrich Co. and used as received. GLC analyses were conducted with a Shimadzu GC-2014 or GC-2025 equipped with a ULBON HR-1 glass capillary column (Shinwa Chemical Industries) and an FID detector. Recycle preparative gel permeation chromatography (GPC) was conducted with a JAI LC-9101 using $CHCl_3$ as the eluent. Electron ionization (EI) high-resolution mass spectra were recorded on time-of-flight mass spectrometer (TOF) at the Global Facility Center, Hokkaido University. Fast atom bombardment (FAB) high-resolution mass spectrum was recorded on TOF at the Research Faculty of Agriculture, Hokkaido University

Preparation of CF_3-Substituted Allenes.

Preparation of (4-(3,3,3-trifluoroprop-1-en-1-ylidene)cyclohexyl)benzene (1a) (Procedure A).[16, 17]

In a vacuum dried 300 mL two necked round-bottomed flask, 1.6 M solution of *n*-BuLi in hexane (25 mL, 40.0 mmol) was added dropwise to a solution of diisopropylamine (5.6 mL, 40.0 mmol) in THF (30 mL) at 0 °C under nitrogen atmosphere. The mixture was stirred for 1 h at that temperature. The lithium diisopropylamine (LDA) mixture was cooled to –78 °C, and 2-bromo-3,3,3-trifluoropropene (2.1 mL, 20.0 mmol) in THF (10 mL) was slowly added at –78 °C. After the solution was stirred for 1 h, 4-phenylcyclohexanone (3.49 g, 20.0 mmol) in THF (10 mL) was added and the mixture was stirred for 2.5 h at that temperature. The reaction mixture was quenched with 1 M HCl (100 mL) at 0 °C and extracted with EtOAc three times. The combined organics were washed with saturated aqueous NaCl, dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified by flash silica gel column chromatography (SiO_2, EtOAc/hexane, 0:100–11:89). The product was obtained in 67% yield (3.57 g, 13.3 mmol).

In a vacuum dried 200 mL two necked round-bottomed flask, Et_3N (2.2 mL, 16.0 mmol) was added dropwise to a solution of alcohol (3.57 g, 13.3 mmol), methanesulfonyl chloride (1.1 mL, 14.7 mmol), 4-dimethylaminopyridine (81.8 mg, 0.67 mmol) in CH_2Cl_2 (53 mL) at 0 °C under nitrogen atmosphere. The solution was stirred for 16 h at room temperature. The reaction mixture was quenched with saturated aqueous NH_4Cl (40 mL) at 0 °C and extracted with CH_2Cl_2 three times. The combined organics were washed with saturated

aqueous NaCl, dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified by flash silica gel column chromatography (SiO_2, EtOAc/hexane, 0:100–15:85). The product was obtained in 61% yield (2.79 g, 8.1 mmol).

In a vacuum dried 300 mL two necked round-bottomed flask, Et_2Zn (24.2 mL, 24.2 mmol, 1.0 M in toluene) was added dropwise to a solution of the methanesulfonyl compound (2.79 g, 8.1 mmol) and $Pd(PPh_3)_4$ (468.5 mg, 0.41 mmol) in THF (82 mL) at 0 °C under nitrogen atmosphere. The solution was stirred for 2.5 h at room temperature. The reaction mixture was quenched with saturated aqueous NH_4Cl (66 mL) at 0 °C, filtered through celite, extracted with EtOAc three times. The combined organics were washed with saturated aqueous NaCl, dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified by flash silica gel column chromatography (SiO_2, hexane only). **1a** was obtained in 45% yield (924.5 mg, 3.7 mmol) as a white solid. ^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.64 (dq, *J* = 3.7, 12.9 Hz, 2H), 2.00–2.09 (m, 2H), 2.28 (tt, *J* = 4.3, 13.5 Hz, 2H), 2.54 (d, *J* = 14.1 Hz, 2H), 2.65 (tt, *J* = 3.9, 12.2 Hz, 1H), 5.32–5.40 (m, 1H), 7.18–7.24 (m, 3H), 7.28–7.34 (m, 2H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 30.2 (*C*H_2), 34.0 (*C*H_2), 43.5 (*C*H), 83.7 (q, *J* = 39.0 Hz, *C*H), 108.9 (*C*), 123.0 (q, *J* = 271.6 Hz, *C*), 126.3 (*C*H), 126.7 (*C*H), 128.5 (*C*H), 146.0 (*C*), 199.9 (q, *J* = 6.0 Hz, *C*). ^{19}F NMR (373 MHz, $CDCl_3$, δ): –61.0 (s, 3F). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{15}H_{15}F_3$, 252.1126; found, 252.1127.

1,1-Dimethyl-4-(3,3,3-trifluoroprop-1-en-1-ylidene)cyclohexane (**1b**). **1b** was prepared from the corresponding ketone according to the procedure A described above. ^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.95 (s, 3H), 0.96 (s, 3H), 1.43 (t, *J* = 6.3 Hz, 4H), 2.17–2.30 (m, 4H), 5.22–5.30 (m, 1H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 26.3 (*C*H_2), 27.9 (*C*H_3), 29.9 (*C*), 39.2 (*C*H_2), 83.2 (q, *J* = 39.0 Hz, *C*H), 109.8 (*C*), 123.1 (q, *J* = 271.3 Hz, *C*), 199.7 (q, *J* = 5.7 Hz, *C*). ^{19}F NMR (373 MHz, $CDCl_3$, δ): –61.1 (d, *J* = 7.1 Hz, 3F). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{11}H_{15}F_3$, 204.1126; found, 204.1126.

Trimethyl[4-methyl-2-(trifluoromethyl)penta-2,3-dien-1-yl]silane (**1c**). **1c** was prepared from the corresponding ketone according to the procedure A described above. Me_3SiCH_2ZnCl (0.49 M in THF) was used instead of Et_2Zn (1.0 M in toluene). After purification by flash silica gel column chromatography, **1c** was further purified by GPC. ^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.04 (s, 9H), 1.40 (s, 2H), 1.75 (s, 6H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): –1.7 (*C*H_3), 14.7 (*C*H_2), 20.1 (*C*H_3), 93.2 (q, *J* = 34.6 Hz, *C*), 102.1 (*C*), 124.2 (q, *J* = 274.8 Hz, *C*), 200.5 (q, *J* = 4.1 Hz, *C*). ^{19}F NMR (373 MHz, $CDCl_3$, δ): –65.9 (s, 3F). HRMS–FAB (*m*/*z*): $[M]^+$ calcd for $C_{10}H_{17}F_3Si$, 222.1052; found, 222.1056.

(1,1,1-Trifluoro-4-methylpenta-2,3-dien-2-yl)benzene (**1d**). **1d** was prepared from the corresponding ketone according to the procedure A described above. PhZnCl (0.29 M in THF) was used instead of Et_2Zn (1.0 M in toluene). ^{1}H NMR (396 MHz, $CDCl_3$, δ): 1.90 (s, 6H), 7.25–7.31 (m, 1H), 7.32–7.42 (m, 4H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 19.5 (*C*H_3), 99.4 (q, *J* = 34.0 Hz, *C*), 105.0 (*C*), 123.7 (q, *J* = 275.4 Hz, *C*), 127.1 (*C*H), 127.7 (*C*H), 128.6 (*C*H), 131.2 (*C*), 202.3 (q, *J* = 3.8 Hz, *C*). ^{19}F NMR (373 MHz, $CDCl_3$, δ): –61.0 (s, 3F). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{12}H_{11}F_3$, 212.0813; found, 212.0812.

1-Methoxy-4-(1,1,1-trifluoro-4-methylpenta-2,3-dien-2-yl)benzene (**1e**). **1e** was prepared from the corresponding ketone according to the procedure A described above. {*p*-C_6H_4}ZnCl (0.50 M in THF) was used instead of Et_2Zn (1.0 M in toluene). After purification by flash silica gel column chromatography, **1e** was further purified by GPC. ^{1}H NMR (396 MHz, $CDCl_3$, δ): 1.89 (s, 6H), 3.82 (s, 3H), 6.85–6.91 (m, 2H), 7.29–7.35 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 19.7 (*C*H_3), 55.3 (*C*H_3), 98.8 (q, *J* = 33.5 Hz, *C*), 104.7 (*C*), 114.0 (*C*H), 123.3 (*C*), 123.4 (q, *J* = 275.3 Hz, *C*), 128.3 (*C*H), 159.2 (*C*), 201.6 (q, *J* = 4.2 Hz, *C*). ^{19}F NMR (373 MHz, $CDCl_3$, δ): –61.2 (s, 3F). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{13}H_{13}F_3O$, 242.0919; found, 242.0923.

1-(1,1,1-Trifluoro-4-methylpenta-2,3-dien-2-yl)naphthalene (**1f**). **1f** was prepared from the corresponding ketone according to the procedure A described above. (1-Naphthyl)ZnCl (0.50 M in THF) was used instead of Et_2Zn (1.0 M in toluene). ^{1}H NMR (396 MHz, $CDCl_3$, δ): 1.87 (s, 6H), 7.46–7.57 (m, 4H), 7.85–7.89 (m, 2H), 8.09 (d, *J* = 8.3 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 19.5 (*C*H_3), 95.3 (q, *J* = 35.8 Hz, *C*), 102.8 (*C*), 123.6 (q, *J* = 275.3 Hz, *C*), 125.16 (*C*H), 125.22 (*C*H), 126.0 (*C*H), 126.4 (*C*H), 127.8 (*C*H), 128.4 (*C*H), 128.9 (*C*H), 132.3 (*C*), 133.8 (*C*), 203.0 (d, *J* = 2.9 Hz, *C*). One quaternary carbon atom not observed due to signal overlapping. ^{19}F NMR (373 MHz, $CDCl_3$, δ): –62.7 (s, 3F). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{16}H_{13}F_3$, 262.0969; found, 262.0972.

(6,6,6-Trifluorohexa-3,4-dien-1-yl)benzene (**1g**). **1g** was prepared from the corresponding aldehyde according to the procedure A described above. After purification by flash silica gel column chromatography, **1g** was further purified by Kugelrohr distillation. ^{1}H NMR (401 MHz, $CDCl_3$, δ): 2.40–2.48 (m, 2H), 2.76 (t, *J* = 7.8 Hz, 2H), 5.37–5.45 (m, 1H), 5.67–5.76 (m, 1H), 7.16–7.24 (m, 3H), 7.27–7.33 (m, 2H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 29.2 (*C*H_2), 34.7 (*C*H_2), 86.2 (q, *J* = 39.0 Hz, *C*H), 97.7 (*C*), 122.8 (q, *J* = 271.3 Hz, *C*), 126.2 (*C*H), 128.4 (*C*H), 146.1 (*C*), 205.2 (q, *J* = 5.7 Hz, *C*). ^{19}F NMR (373 MHz, $CDCl_3$, δ): –61.1 (s, 3F). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{12}H_{11}F_3$, 212.0813; found, 212.0813.

(4,4,4-Trifluorobuta-1,2-dien-1-yl)cyclohexane (**1h**). **1h** was prepared from the corresponding aldehyde according to the procedure described above. After purification by flash silica gel column chromatography, **1h** was further purified by Kugelrohr distillation. ^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.07–1.21 (m, 3H), 1.22–1.36 (m, 2H), 1.61–1.69 (m, 1H), 1.70–1.82 (m, 4H), 2.07–2.18 (m, 1H), 5.44 (double quint, *J* = 3.1, 6.0 Hz, 1H), 5.63–5.70 (m, 1H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 25.8 (*C*H_2), 25.9 (*C*H_2), 32.4 (*C*H_2), 36.5 (*C*H), 86.5 (q, *J* = 39.0 Hz, *C*H), 104.1 (*C*H), 122.9 (q, *J* = 271.3 Hz, *C*), 204.4 (q, *J* = 7.3 Hz, *C*). ^{19}F NMR (373 MHz, $CDCl_3$, δ): –61.0 (t, *J* = 5.8 Hz, 3F). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{10}H_{13}F_3$, 190.0969; found, 190.0976.

(6,6,6-Trifluoro-3-methylhexa-3,4-dien-1-yl)benzene (**1i**). **1i** was prepared from the corresponding ketone according to the procedure A described above. After purification by flash silica gel column chromatography, **1i** was further purified by Kugelrohr distillation. ^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.82 (d, *J* = 7.8 Hz, 3H), 2.32–2.38 (m, 2H), 2.71–2.77 (m, 2H), 5.29–5.38 (m, 1H), 7.16–7.23 (m, 3H) , 7.26–7.32 (m, 2H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 18.3 (*C*H_3), 33.4 (*C*H_2), 34.8 (*C*H_2), 85.4 (q, *J* = 38.9 Hz, *C*H), 107.5 (*C*), 122.9 (q, *J* = 271.6 Hz, *C*), 126.1 (*C*H), 128.3 (*C*H), 128.4 (*C*H), 141.1 (*C*), 202.8 (q, *J* = 6.0 Hz, *C*). ^{19}F NMR (373 MHz, $CDCl_3$, δ): –61.1 (s, 3F). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{13}H_{13}F_3$, 226.0969; found, 226.0968.

Preparation of (6,6,6-trifluorohexa-3,4-diene-1,5-diyl)dibenzene (1j).[18-20]

In a vacuum dried 300 mL two necked round-bottomed flask, 1.6 M solution of *n*-BuLi in hexane (13.5 mL, 21.0 mmol) was added dropwise to a solution of alkyne (2.41 mL, 22.0 mmol) in anhydrous THF (80 mL) at –78 °C under nitrogen atmosphere. The solution was stirred for 15 min at that temperature before the addition of 3-phenylpropionaldehyde (2.63 mL, 20.0 mmol). The mixture was allowed to warm to 0 °C gradually and stirred for an additional hour. The reaction mixture was quenched with 1 M HCl (50 mL) at 0 °C and extracted with Et_2O three times. The combined organics were washed with saturated aqueous NaCl, dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified by flash column chromatography (SiO_2, EtOAc/hexane, 0:100–15:85). The product was obtained in 97% yield (4.60 g, 19.5 mmol).

In a vacuum dried 200 mL two necked round-bottomed flask, $SOCl_2$ (1.6 mL, 21.5 mmol) was added dropwise to a solution of propargyl alcohol (4.60 g, 19.5 mmol) and pyridine (1.9 mL, 23.4 mmol) in anhydrous CH_2Cl_2 (30 mL) at 0 °C under nitrogen atmosphere. The reaction mixture was stirred for 10 min at that temperature. The mixture was allowed to warm up to room temperature and stirred overnight at room temperature. The mixture was diluted with Et_2O (40 mL) and washed with 1 M HCl (30 mL × 3). The water layer was extracted with Et_2O three times. The combined organics were washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, filtered and evaporated to dryness. The crude product was purified by flash column chromatography (SiO_2, EtOAc/hexane, 0:100–3:97). The product was obtained in 38% yield (1.90 g, 7.46 mmol).

In a vacuum dried 200 mL two necked round-bottomed flask, propargyl chloride (1.90 g, 7.46 mmol) and CF_3SiMe_3 (1.67 mL, 11.3 mmol) were added dropwise to a solution of Copper(I) 2-thiophenecarboxylate (71.5 mg, 0.375 mmol) and KF (658.6 mg, 11.3 mmol) in anhydrous THF (45 mL) under nitrogen atmosphere. The mixture was stirred at 60 °C (heating plate with aluminum blocks) for 23 h. The solution was poured into water (45 mL) and the mixture was extracted with Et_2O three times. The combined extracts were washed with saturated aqueous NaCl, filtered and evaporated to dryness. After purification by flash silica gel column chromatography (SiO_2, hexane only), the product was further purified by GPC. **1j** was obtained in 9% yield (201.5 mg, 0.70 mmol) as a white solid. ^{1}H NMR (401 MHz, $CDCl_3$, δ): 2.48–2.65 (m, 2H), 2.77–2.90 (m, 2H), 5.97 (octet, *J* = 3.3 Hz, 1H), 7.18–7.35 (m, 10H). $^{13}C\{^1H\}$ NMR (99 MHz, $CDCl_3$, δ): 29.8 (*C*H_2), 34.8 (*C*H_2), 99.3 (*C*H), 102.1 (q, *J* = 34.3 Hz, *C*), 123.4 (q, *J* = 275.4 Hz, *C*), 126.2 (*C*H), 126.8 (*C*H), 127.9 (*C*H), 128.5 (*C*H), 128.6 (*C*H), 129.9 (*C*), 140.6 (*C*), 204.3 (q, *J* = 4.1 Hz, *C*). ^{19}F NMR (373 MHz, $CDCl_3$, δ): –60.9 (s, 3F). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{18}H_{15}F_3$, 288.1126; found, 288.1128.

Preparation of (1,1,1-trifluorobuta-2,3-dien-2-yl)benzene (1k).[21]

In a vacuum dried 200 mL two necked round-bottomed flask, CBr_4 (3.78 g, 11.4 mmol) was quickly added to a solution of PPh_3 (5.80 g, 22.1 mmol) in toluene (28 mL) under nitrogen atmosphere. After stirring for 30 min, 2,2,2-trifluoroacetophenone (1.36 mL, 10.0 mmol) was dropwise added over 15 min. The mixture was stirred for 30 min and then refluxed (heating plate with aluminum blocks) for 18 h. The reaction mixture was allowed to cool to room temperature, at which point hexane (20 mL) was added to precipitate salts. The suspension was filtered through Celite®, washing with hexane. Then the filtrate was quenched with water and extracted with hexane three times. The combined organics were washed with saturated aqueous NaCl, dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified by flash silica gel column chromatography (SiO_2, hexane only). The product was obtained in 76% yield (2.51 g, 7.61 mmol).

In a vacuum dried 200 mL two necked round-bottomed flask, 1.6 M solution of *n*-BuLi in hexane (4.76 mL, 7.61 mmol) was added dropwise to a solution of the *gem*-dibromo compound (2.51 g, 7.61 mmol) in THF (76 mL) at –78 °C under nitrogen atmosphere and the mixture was stirred for 40 min at that temperature. Paraformaldehyde (933.4 mg, 31.1 mmol) was added and let warm to room temperature while stirring 17 h. Then the reaction mixture was cooled to 0 ºC. Et_3N (1.6 mL, 11.4 mmol) was added and stirred for 30 min, followed by dropwise addition of MsCl (1.2 mL, 15.2 mmol) and stirring for 2.5 h at this temperature. The reaction mixture was quenched with 1 M HCl (36 mL) at 0 °C and extracted with Et_2O three times. The combined organics were washed with saturated aqueous NaCl, dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified by flash silica gel column chromatography (SiO_2, EtOAc/hexane, 3:97–20:80). The product was obtained in 60% yield (1.65 g, 4.59 mmol).

The obtained methanesulfonyl compound (1.65 g, 4.59 mmol) and LiBr (397.2 mg, 4.57 mmol) were placed in a vacuum dried 200 mL two necked round-bottomed flask. Then DMF (9.2 mL) was added under nitrogen atmosphere, and the mixture was heated to 50 ºC (heating plate with aluminum blocks) for 5 hours. Upon cooling to room temperature, Zn powder (334.8 mg, 5.12 mmol) was added and stirred for 22 hours. The reaction mixture was quenched with 1 M HCl (11 mL) at 0 °C and extracted with Et_2O three times. The combined organics were washed with saturated aqueous NaCl, dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified by flash column chromatography (SiO_2, pentane only). The product was further purified by Kugelrohr distillation. **1k** was obtained in 47% yield (396.5 mg, 2.15 mmol) as a colorless oil. ^{1}H NMR (396 MHz, $CDCl_3$, δ): 5.54 (q, *J* = 3.4 Hz, 2H), 7.28–7.48 (m, 5H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 83.4 (*C*H_2), 101.8 (q, *J* = 34.8 Hz, *C*), 123.4 (q, *J* = 275.0 Hz, *C*), 127.0 (*C*H), 128.2 (*C*H), 128.7 (*C*H), 129.2 (*C*H), 208.5 (q, *J* = 3.8 Hz, *C*). ^{19}F NMR (373 MHz, $CDCl_3$, δ): –61.0– –60.9 (m, 3F). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{10}H_7F_3$, 184.0500; found, 184.0504.

General Borylation Procedure and Product Characterizations

Procedure for 2-[3,3-difluoro-1-(4-phenylcyclohexylidene)allyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a). CuCl (2.5 mg, 0.025 mmol), PPh_3 (6.7 mg, 0.026 mmol), **1a** (126.1 mg, 0.50 mmol) and bis(pinacolato)diboron (**2**) (190.3 mg, 0.75 mmol) were placed in an oven-dried reaction vial. The vial was moved to an argon-filled glovebox. NaOMe (40.5 mg, 0.75 mmol) was placed in a reaction vial. Then the vial was capped with a rubber septum and removed from the glovebox. Dry THF (1 mL) was added in the vial through the rubber septum using a syringe. After stirring for 3 h at 30 ºC (heating plate with aluminum blocks), the reaction mixture was passed

through a short silica gel column (Φ: 10 mm, the height of the silica-gel column: 30 mm) eluting with Et_2O. The crude material was purified by flash silica gel column chromatography (SiO_2, Et_2O/hexane, 0:100–6:94) to give the corresponding borylation product **3a** as a white solid (83%, 150.0 mg, 0.415 mmol). The product contains a small amount of byproducts. ^{1}H NMR (396 MHz, $CDCl_3$, δ): 1.31 (s, 12H), 1.45–1.68 (m, 2H), 1.93–2.05 (m, 3H), 2.12–2.23 (m, 1H), 2.70–2.81 (m, 2H), 2.93–3.00 (m, 1H), 5.15 (dd, *J* = 3.2, 27.3 Hz, 1H), 7.15–7.21 (m, 3H) , 7.24–7.31 (m, 2H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 24.75 (*C*H$_3$), 24.81 (*C*H$_3$), 31.3 (*C*H$_2$), 34.7 (*C*H$_2$), 34.9 (*C*H$_2$), 35.6 (*C*H$_2$), 44.4 (CH), 79.9 (dd, *J* = 17.0, 25.5 Hz, *C*H), 112.5 (brs, B–C), 126.0 (*C*H), 126.7 (*C*H), 128.3 (*C*H), 146.3 (*C*), 154.1 (d, *J* = 6.5 Hz, *C*), 155.6 (dd, *J* = 288.9, 294.6 Hz, *C*). ^{19}F NMR (373 MHz, $CDCl_3$, δ): –89.6 (d, *J* = 34.3 Hz, 1F), –85.0 (dd, *J* = 27.4, 36.7 Hz, 1F). HRMS-EI (*m*/*z*): [M]$^+$ calcd for $C_{21}H_{27}{}^{10}BF_2O_2$, 359.2109; found, 359.2104.

2-[1-(4,4-Dimethylcyclohexylidene)-3,3-difluoroallyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3b**). The reaction was conducted with 100.8 mg (0.49 mmol) of **1b** for 2.5 h. The product **3b** was obtained in 89% yield (136.9 mg, 0.44 mmol). ^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.95 (s, 6H), 1.30 (s, 12H), 1.35 (t, *J* = 6.3 Hz, 2H), 1.40 (t, *J* = 6.3 Hz, 2H), 2.21 (t, *J* = 6.3 Hz, 2H), 2.41 (t, *J* = 6.3 Hz, 2H), 5.11 (dd, *J* = 3.2, 27.7 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 24.8 (*C*H$_3$), 27.4 (*C*H$_2$), 28.0 (*C*H$_3$), 30.2 (*C*), 30.8 (*C*H$_2$), 40.0 (*C*H$_2$), 40.8 (*C*H$_2$), 80.0 (dd, *J* = 17.3, 25.0 Hz, *C*H), 83.4 (*C*), 111.8 (brs, B–C), 155.6 (t, *J* = 290.8 Hz, *C*), 155.6 (t, *J* = 6.3 Hz, *C*). ^{19}F NMR (373 MHz, $CDCl_3$, δ): –90.1– –90.0 (m, 1F), –85.4 (dd, *J* = 27.4, 39.0 Hz, 1F). HRMS-EI (*m*/*z*): [M]$^+$ calcd for $C_{17}H_{27}{}^{10}BF_2O_2$, 311.2109; found, 311.2107.

[2-(Difluoromethylene)-4-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-en-1-yl]trimethylsilane (**3c**). The reaction was conducted with 55.3 mg (0.25 mmol) of **1c** for 8 h. The product **3c** was obtained in 79% yield (64.9 mg, 395 mmol). ^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.00 (s, 9H), 1.26 (s, 12H), 1.40–1.44 (m, 2H), 1.76 (d, *J* = 1.6 Hz, 3H), 2.00 (s, 3H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): –1.2 (*C*H$_3$), 18.0 (*C*H$_2$), 23.5 (d, *J* = 1.9 Hz, *C*H$_3$), 24.0 (*C*H$_3$), 24.7 (*C*H$_3$), 82.9 (*C*), 89.3 (t, *J* = 19.8 Hz, *C*), 150.9 (dd, *J* = 282.8, 285.6 Hz, *C*), 151.9 (*C*). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation. ^{19}F NMR (373 MHz, $CDCl_3$, δ): –97.9 (d, *J* = 54.8 Hz, 1F), –93.7 (d, *J* = 54.8 Hz, 1F). HRMS-EI (*m*/*z*): [M]$^+$ calcd for $C_{16}H_{29}{}^{10}BF_2O_2Si$, 329.2034; found, 329.2026.

2-(1,1-Difluoro-4-methyl-2-phenylpenta-1,3-dien-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3d**). The reaction was conducted with 105.4 mg (0.50 mmol) of **1d** for 4 h. The product **3d** was obtained in 91% yield (144.9 mg, 0.45 mmol). ^{1}H NMR (396 MHz, $CDCl_3$, δ): 1.11 (s, 12H), 1.75 (d, *J* = 1.2 Hz, 3H), 2.11 (s, 3H), 7.19 (tt, J = 2.2, 7.0 Hz, 1H), 7.25–7.35 (m, 4H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 23.0 (*C*H$_3$), 24.1 (*C*H$_3$), 24.4 (*C*H$_3$), 83.0 (*C*), 94.6 (dd, *J* = 13.2, 23.6 Hz, *C*), 126.6 (*C*H), 128.0 (*C*H), 128.3 (t, *J* = 3.8 Hz, *C*H), 134.9 (t, *J* = 4.7 Hz, *C*), 152.3 (dd, *J* = 286.1, 297.4 Hz, *C*), 154.6 (*C*). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation. ^{19}F NMR (373 MHz, $CDCl_3$, δ): –92.5 (d, *J* = 36.6 Hz, 1F), –86.5 (d, *J* = 38.8 Hz, 1F). HRMS-EI (*m*/*z*): [M]$^+$ calcd for $C_{18}H_{23}{}^{10}BF_2O_2$, 319.1796; found, 319.1796.

2-[1,1-Difluoro-2-(4-methoxyphenyl)-4-methylpenta-1,3-dien-3-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3e**). The reaction was conducted with 120.2 mg (0.50 mmol) of **1e** for 5 h. The product **3e** was obtained in 84% yield (146.3 mg, 0.42 mmol). ^{1}H NMR (396 MHz, $CDCl_3$, δ): 1.12 (s, 12H), 1.74 (d, *J* = 1.6 Hz, 3H), 2.10 (s, 3H), 3.79 (s, 3H), 6.80–6.86 (m, 2H), 7.22–7.27 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 22.9 (*C*H$_3$), 24.1 (*C*H$_3$), 24.4 (*C*H$_3$), 55.1 (*C*H$_3$), 83.0 (*C*), 94.0 (dd, *J* = 13.4, 23.9 Hz, *C*), 113.4 (*C*H), 127.1 (t, *J* = 4.8 Hz, *C*), 129.3 (t, *J* = 3.8 Hz, *C*H), 152.1 (dd, *J* = 285.5, 296.1 Hz, *C*), 154.1 (*C*), 158.2 (*C*). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation. ^{19}F NMR (373 MHz, $CDCl_3$, δ): –93.7 (d, *J* = 41.0 Hz, 1F), –87.9 (d, *J* = 38.8 Hz, 1F). HRMS-EI (*m*/*z*): [M]$^+$ calcd for $C_{19}H_{25}{}^{10}BF_2O_3$, 349.1901; found, 349.1911.

2-[1,1-Difluoro-4-methyl-2-(naphthalen-1-yl)penta-1,3-dien-3-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3f**). The reaction was conducted with 131.1 mg (0.50 mmol) of **1f** for 25 h. The product **3f** was obtained in 85% yield (158.1 mg, 0.43 mmol). ^{1}H NMR (401 MHz, $CDCl_3$, δ): 0.92 (s, 12H), 1.90 (d, *J* = 2.4 Hz, 3H), 2.08 (s, 3H), 7.31–7.53 (m, 4H), 7.72–7.84 (m, 2H), 8.09 (dd, *J* = 3.8, 8.2 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 23.2 (d, *J* = 2.0 Hz, *C*H$_3$), 24.2 (*C*H$_3$), 24.4 (*C*H$_3$), 83.0 (*C*), 94.4 (dd, *J* = 17.7, 23.5 Hz, *C*), 125.0 (*C*H), 125.5 (*C*H), 125.6 (*C*H), 126.4 (d, *J* = 1.9 Hz, *C*H), 127.9 (*C*H), 128.0 (d, *J* = 2.8 Hz, *C*H), 128.1 (*C*H), 131.3 (*C*), 132.5 (t, *J* = 3.3 Hz, *C*), 133.6 (*C*), 151.5 (dd, *J* = 289.8, 293.7 Hz, *C*), 152.0 (*C*). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation. ^{19}F NMR (373 MHz, $CDCl_3$, δ): –88.3 (d, *J* = 36.6 Hz, 1F), –87.7 (d, *J* = 34.3 Hz, 1F). HRMS-EI (*m*/*z*): [M]$^+$ calcd for $C_{22}H_{25}{}^{10}BF_2O_2$, 369.1952; found, 369.1959.

(Z)-2-(1,1-Difluoro-6-phenylhexa-1,3-dien-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*Z*)-**3g**]. The reaction was conducted with 106.3 mg (0.50 mmol) of **1g** for 5 h. The product (*Z*)-**3g** was obtained in 50% yield (80.1 mg, 0.25 mmol, *Z*/*E* = 94/6) with small amount of byproducts. *Z*/*E* ratio was determined by ^{19}F NMR analysis of crude mixture. ^{1}H NMR (396 MHz, $CDCl_3$, δ): 1.28 (s, 12H), 2.44 (q, *J* = 7.8 Hz, 2H), 2.69–2.76 (m, 2H), 4.98 (dd, *J* = 1.2, 26.5 Hz, 1H), 6.36 (t, *J* = 6.9 Hz, 1H), 7.16–7.22 (m, 3H), 7.26–7.32 (m, 2H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 24.6 (*C*H$_3$), 31.8 (*C*H$_2$), 34.8 (*C*H$_2$), 78.1 (dd, *J* = 18.4, 26.9 Hz, *C*H), 83.7 (*C*), 126.0 (*C*H), 128.3 (*C*H), 128.4 (*C*H), 141.5 (*C*), 146.7 (d, *J* = 4.7 Hz, *C*H), 155.1 (dd, *J* = 289.4, 296.0 Hz, *C*). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation. ^{19}F NMR (373 MHz, $CDCl_3$, δ): –87.1 (d, *J* = 29.5 Hz, 1F), –82.4 (t, *J* = 30.5 Hz, 1F). HRMS-EI (*m*/*z*): [M]$^+$ calcd for $C_{18}H_{23}{}^{10}BF_2O_2$, 319.1796; found, 319.1790.

2-(1-Cyclohexyl-4,4-difluorobuta-1,3-dien-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3h**). The reaction was conducted with 95.1 mg (0.50 mmol) of **1h** for 5.5 h. The product **3h** was purified by GPC and obtained in 49% yield (73.8 mg, 0.25 mmol, *Z*/*E* = 69/31). *Z*/*E* ratio was determined by ^{19}F NMR analysis of crude mixture. For major isomer: ^{1}H NMR (396 MHz, $CDCl_3$, δ): 1.01–1.24 (m, 5H), 1.28 (s, 12H), 1.58–1.76 (m, 5H), 2.21–2.32 (m, 1H), 5.05 (dq, *J* = 1.5, 26.8 Hz, 1H), 6.08 (d, *J* = 9.5 Hz, 1H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 24.5 (*C*H$_3$), 25.7 (*C*H$_2$), 25.7 (*C*H$_2$), 32.0 (*C*H$_2$), 38.6 (*C*H), 78.1 (dd, *J* = 17.9, 26.4 Hz, *C*H), 83.5 (*C*), 152.9 (d, *J* = 4.9 Hz, *C*H), 155.6 (t, *J* = 292.7 Hz, *C*). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation. ^{19}F NMR (373 MHz, $CDCl_3$, δ): –87.7 (d, *J* = 32.1 Hz, 1F), –82.9 (dd, *J* = 27.6, 32.1 Hz, 1F). HRMS-EI (*m*/*z*): [M]$^+$ calcd for $C_{16}H_{25}{}^{10}BF_2O_2$,

297.1952; found, 297.1952. For minor isomer: ^{1}H NMR (396 MHz, $CDCl_3$, δ): 1.01–1.24 (m, 5H), 1.31 (s, 12H), 1.58–1.76 (m, 5H), 2.33–2.42 (m, 1H), 4.91 (dd, *J* = 3.0, 27.1 Hz, 1H), 5.88 (d, *J* = 9.5 Hz, 1H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 24.7 (*C*H$_3$), 25.8 (*C*H$_2$), 25.9 (*C*H$_2$), 33.2 (*C*H$_2$), 40.6 (*C*H), 83.7 (*C*), 84.5 (dd, *J* = 16.0, 26.4 Hz, *C*H), 151.0 (dd, *J* = 3.9, 8.9 Hz, *C*), 155.2 (t, *J* = 292.2 Hz, *C*). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation. ^{19}F NMR (373 MHz, $CDCl_3$, δ): –91.0– –90.9 (m, 1F), –85.1 (dd, *J* = 26.1, 37.7 Hz, 1F).

2-(1,1-Difluoro-4-methyl-6-phenylhexa-1,3-dien-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3i**). The reaction was conducted with 113.0 mg (0.50 mmol) of **1i** for 6 h. The product **3i** was obtained in 87% yield (145.7 mg, 0.44 mmol, *E*/*Z* = 42/58). *E*/*Z* ratio was determined by ^{19}F NMR analysis of crude mixture. For major isomer: ^{1}H NMR (396 MHz, $CDCl_3$, δ): 1.29 (s, 12H), 1.82 (s, 3H), 2.55–2.62 (m, 2H), 2.65–2.77 (m, 2H), 5.06 (dt, *J* = 3.5, 27.2 Hz, 1H), 7.16–7.31 (m, 5H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 19.9 (*C*H$_3$), 24.85 (*C*H$_3$), 35.7 (*C*H$_2$), 40.9 (*C*H$_2$), 80.7 (dd, *J* = 17.0, 25.5 Hz, *C*H), 83.5 (*C*), 125.8 (*C*H), 128.2–128.4 (m, *C*H), 142.1 (*C*), 151.9 (d, *J* = 5.7 Hz, *C*), 155.2 (dd, *J* = 288.9, 294.6 Hz, *C*). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation. ^{19}F NMR (373 MHz, $CDCl_3$, δ): –89.5 (d, *J* = 36.6 Hz, 1F), –84.5– –84.3 (m, 1F). HRMS-EI (*m*/*z*): [M]$^+$ calcd for $C_{19}H_{25}{}^{10}BF_2O_2$, 333.1952; found, 333.1950. For minor isomer: ^{1}H NMR (396 MHz, $CDCl_3$, δ): 1.32 (s, 12H), 2.01 (s, 3H), 2.36–2.43 (m, 2H), 2.65–2.77 (m, 2H), 5.06 (dt, *J* = 3.5, 27.2 Hz, 1H), 7.16–7.31 (m, 5H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 22.5 (*C*H$_3$), 24.80 (*C*H$_3$), 33.9 (*C*H$_2$), 37.7 (*C*H$_2$), 80.1 (dd, *J* = 17.4, 25.9 Hz, *C*H), 83.6 (*C*), 125.9 (*C*H), 128.2–128.4 (m, *C*H), 141.7 (*C*), 150.9 (d, *J* = 6.6 Hz, *C*), 155.5 (dd, *J* = 288.9, 293.7 Hz, *C*). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation. ^{19}F NMR (373 MHz, $CDCl_3$, δ): –89.7 (d, *J* = 36.6 Hz, 1F), –84.5– –84.3 (m, 1F).

2-(1,1-Difluoro-2,6-diphenylhexa-1,3-dien-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3j**). The reaction was conducted with 144.8 mg (0.50 mmol) of **1j** for 6.5 h. The product **3j** was purified by GPC and obtained in 45% yield (90.4 mg, 0.23 mmol, *Z*/*E* = 79/21) with small amount of byproducts. *Z*/*E* ratio was determined by ^{19}F NMR analysis of crude mixture. For major isomer: ^{1}H NMR (396 MHz, $CDCl_3$, δ): 1.17 (s, 12H), 2.38 (q, *J* = 7.8 Hz, 2H), 2.62–2.71 (m, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 7.05–7.33 (m, 10H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 24.4 (*C*H$_3$), 32.6 (*C*H$_2$), 34.6 (*C*H$_2$), 83.5 (*C*), 92.2 (dd, *J* = 14.2, 23.7 Hz, *C*), 125.9 (*C*H), 126.7 (*C*H), 127.9–128.4(m, *C*H), 128.5 (*C*H), 129.5 (t, *J* = 2.8 Hz, *C*H), 134.3 (t, *J* = 4.7 Hz, *C*), 141.5 (*C*), 150.5 (*C*H), 152.0 (dd, *J* = 287.5, 297.9 Hz, *C*). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation. ^{19}F NMR (373 MHz, $CDCl_3$, δ): –91.2 (d, *J* = 34.3 Hz, 1F), –85.2 (d, *J* = 34.3 Hz, 1F). HRMS-EI (*m*/*z*): [M]$^+$ calcd for $C_{24}H_{27}{}^{10}BF_2O_2$, 395.2109; found, 395.2122. For minor isomer: ^{1}H NMR (396 MHz, $CDCl_3$, δ): 1.18 (s, 12H), 2.38 (q, *J* = 7.8 Hz, 2H), 2.62–2.71 (m, 2H), 6.02–6.16 (m, 1H), 7.05–7.33 (m, 10H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 24.6 (*C*H$_3$), 33.6 (*C*H$_2$), 36.0 (*C*H$_2$), 83.5 (*C*), 92.2 (dd, *J* = 14.2, 23.7 Hz, *C*), 125.8 (*C*H), 127.1 (*C*H), 127.9–128.4 (m, *C*H), 128.6 (*C*H), 129.7 (*C*H), 134.3 (t, *J* = 4.7 Hz, *C*), 141.6 (*C*), 150.5 (*C*H), 152.0 (dd, *J* = 287.5, 297.9 Hz, *C*). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation. ^{19}F NMR (373 MHz, $CDCl_3$, δ): –91.3 (d, *J* = 36.9 Hz, 1F), –88.2 (d, *J* = 36.6 Hz, 1F).

Cross-Coupling Reaction Procedure and Product Characterizations

Procedure for 1-[3,3-difluoro-1-(4-phenylcyclohexylidene)allyl]-4-methoxybenzene (4a).[9c]
$Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 5.0 mol%), SPhos (4.0 mg, 0.010 mmol, 10 mol%), **3a** (36.2 mg, 0.10 mmol) were placed in an oven-dried reaction vial. The flask was then evacuated and backfilled with nitrogen three times. THF (0.21 mL), aqueous NaOH (0.12 mL of 2.5 M solution in H_2O, 0.30 mmol) and 4-bromoanisole (28.5 mg, 0.15 mmol) were added to the flask. The resulting solution was stirred at 60 ºC (heating plate with aluminum blocks) for 25 h. After the reaction, the mixture was extracted with Et_2O, and the organic layer was dried over $MgSO_4$. After filtration, all of the volatiles were removed by rotary evaporator. The crude material was purified by flash silica gel column chromatography (SiO_2, Et_2O/hexane, 0:100–2:98). **4a** was obtained in 75% yield (25.8 mg, 0.076 mmol) as a colorless oil. ^{1}H NMR (396 MHz, $CDCl_3$, δ): 1.40–1.70 (m, 2H), 1.85–2.19 (m, 4H), 2.54–2.62 (m, 1H), 2.68–2.87 (m, 2H), 3.81 (s, 3H), 5.17 (dd, *J* = 4.4, 25.3 Hz, 1H), 6.84–6.89 (m, 2H), 7.07–7.11 (m, 2H), 7.16–7.33 (m, 5H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 31.6 (*C*H$_2$), 35.1 (*C*H$_2$), 35.5 (*C*H$_2$), 44.5 (*C*H), 55.2 (*C*H$_3$), 81.2 (dd, *J* = 14.2, 26.4 Hz, *C*H), 113.4 (*C*H), 122.1 (t, *J* = 4.7 Hz, *C*), 126.1 (*C*H), 126.8 (*C*H), 128.4 (*C*H), 130.2 (*C*H), 132.8 (*C*), 139.9 (dd, *J* = 1.9, 5.6 Hz, *C*), 146.6 (*C*), 155.6 (dd, *J* = 288.0, 298.4 Hz, *C*), 158.2 (*C*). ^{19}F NMR (373 MHz, $CDCl_3$, δ): –87.5 (d, *J* = 29.8 Hz, 1F), –83.3 (dd, *J* = 26.5, 31.0 Hz, 1F). HRMS-EI (*m*/*z*): [M]$^+$ calcd for $C_{22}H_{22}F_2O$, 340.1639; found, 340.1635.

1-[1-(4,4-Dimethylcyclohexylidene)-3,3-difluoroallyl]naphthalene (**4b**). The reaction was conducted with 31.4 mg (0.10 mmol) of **3b** and the corresponding aryl bromide for 18 h. The product **4b** was obtained in 61% yield (19.1 mg, 0.061 mmol). ^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.95 (s, 6H), 1.15 (t, *J* = 6.3 Hz, 2H), 1.51 (q, *J* = 5.5 Hz, 2H), 1.74–1.88 (m, 2H), 2.46 (t, *J* = 6.3 Hz, 2H), 5.32 (dd, *J* = 4.6, 24.8 Hz, 1H), 7.23 (d, *J* = 6.7 Hz, 1H), 7.41–7.49 (m, 3H), 7.75–7.87 (m, 3H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 26.9 (*C*H$_3$), 27.90 (*C*H$_3$), 27.95 (*C*H$_2$), 28.2 (*C*H$_2$), 30.3 (*C*), 40.4 (*C*H$_2$), 40.5 (*C*H$_2$), 81.0 (dd, *J* = 12.8, 27.8 Hz, *C*H), 119.8 (t, *J* = 5.2 Hz, *C*), 125.43 (*C*H), 125.46 (*C*H), 125.6 (*C*H), 125.8 (*C*H), 126.4 (*C*H), 127.1 (*C*H), 128.3 (*C*H), 131.9 (*C*), 133.5 (*C*), 138.5 (*C*), 142.6 (q, *J* = 3.1 Hz, *C*), 155.5 (t, *J* = 293.6 Hz, *C*). ^{19}F NMR (373 MHz, $CDCl_3$, δ): –87.5 (dd, *J* = 4.7, 31.9 Hz, 1F), –83.5 (dd, *J* = 25.2, 29.7 Hz, 1F). HRMS-EI (*m*/*z*): [M]$^+$ calcd for $C_{21}H_{22}F_2$, 312.1690; found, 312.1695.

1-[1-(4,4-Dimethylcyclohexylidene)-3,3-difluoroallyl]-2-methoxybenzene (**4c**). The reaction was conducted with 31.3 mg (0.100 mmol) of **3b** and the corresponding aryl bromide for 27 h. The product **4c** was obtained in 50% yield (14.8 mg, 0.0506 mmol). ^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.94 (s, 3H), 0.95 (s, 3H), 1.17–1.32 (m, 2H), 1.35–1.51 (m, 2H), 1.88–2.02 (m, 2H), 2.30–2.37 (m, 2H), 3.79 (s, 3H), 5.23 (dd, *J* = 4.5, 25.3 Hz, 1H), 6.86–6.94 (m, 2H), 7.00–7.06 (m, 1H), 7.22–7.28 (m, 1H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 26.9 (*C*H$_2$), 27.6 (*C*H$_3$), 27.7 (*C*H$_2$), 28.7 (*C*H$_3$), 30.3 (*C*), 40.2 (*C*H$_2$), 40.4 (*C*H$_2$), 55.5(*C*H$_3$), 80.4 (dd, *J* = 13.3, 27.4 Hz, *C*H), 110.7 (*C*H), 118.1 (t, *J* = 4.8 Hz, *C*H), 120.3 (*C*H), 128.1 (*C*H), 129.3 (*C*), 130.9 (*C*H), 141.7 (dd, *J* = 2.8, 6.6 Hz, *C*), 155.4 (dd, *J* = 287.0, 298.4 Hz, *C*), 157.0 (*C*). ^{19}F NMR (373 MHz, $CDCl_3$, δ): –88.4 (dd, *J* = 4.8, 32.1 Hz, 1F), –85.1 (dd, *J* = 25.0, 32.1

Hz, 1F). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{18}H_{22}F_2O$, 292.1639; found, 292.1638.

1-(1-(4,4-Dimethylcyclohexylidene)-3,3-difluoroallyl)-2-(trifluoromethyl)benzene (**4d**). The reaction was conducted with 31.9 mg (0.102 mmol) of **3b** and the corresponding aryl bromide for 21 h. The product **4d** was obtained in 62% yield (21.0 mg, 0.064 mmol). ^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.93 (s, 3H), 0.95 (s, 3H), 1.08–1.18 (m, 1H), 1.19–1.29 (m, 1H), 1.32–1.49 (m, 2H), 1.70–1.85 (m, 2H), 2.25–2.40 (m, 2H), 5.26 (dd, *J* = 4.8, 24.6 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.34–7.41 (m, 1H), 7.46–7.53 (m, 1H), 7.66 (d, *J* = 7.9 Hz, 1H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 26.6 (*C*H_2), 27.7 (*C*H_3), 28.1 (*C*H_2), 28.4 (*C*H_3), 30.1 (*C*), 39.7 (*C*H_2), 40.0 (*C*H_2), 80.8 (dd, *J* = 12.3, 29.3 Hz, *C*H), 119.3 (t, *J* = 5.2 Hz, *C*), 124.2 (q, *J* = 275.1 Hz, *C*), 126.0 (q, *J* = 5.0 Hz, *C*H), 127.0 (*C*H), 128.7 (q, *J* = 28.6 Hz, *C*), 131.5 (*C*H), 131.6 (*C*H), 139.5 (*C*), 142.0–142.2 (m, *C*), 155.6 (dd, *J* = 287.1, 299.3 Hz, *C*). ^{19}F NMR (373 MHz, $CDCl_3$, δ): –87.6 (d, *J* = 38.0 Hz, 1F), –84.3 (t, *J* = 29.1 Hz, 1F), –60.9 (s, 3F). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{18}H_{19}F_5$, 330.1407; found, 330.1396.

5-[1-(4,4-Dimethylcyclohexylidene)-3,3-difluoroallyl]-1,2,3-trimethoxybenzene (**4e**). The reaction was conducted with 31.2 mg (0.10 mmol) of **3b** and the corresponding aryl bromide for 20 h. The product **4e** was obtained in 83% yield (29.1 mg, 0.083 mmol). ^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.96 (s, 6H), 1.28 (t, *J* = 6.3 Hz, 2H), 1.43 (t, *J* = 6.3 Hz, 2H), 2.11 (t, *J* = 6.3 Hz, 2H), 2.30 (t, *J* = 5.9 Hz, 2H), 3.84 (s, 6H), 3.86 (s, 3H), 5.11 (dd, *J* = 4.0, 25.3 Hz, 1H), 6.33 (s, 2H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 27.5 (*C*H_2), 27.7 (*C*H_2), 28.1 (*C*H_3), 30.3 (*C*), 40.1 (*C*H_2), 40.7 (*C*H_2), 56.0 (*C*H_3), 60.9 (*C*H_3), 80.9 (dd, *J* = 14.7, 26.9 Hz, *C*H), 106.1 (*C*H), 108.8 (*C*), 121.9 (t, *J* = 4.7 Hz, *C*), 136.4 (*C*), 136.5 (*C*), 141.5 (dd, *J* = 1.9, 5.6 Hz, *C*), 152.8 (*C*), 155.4 (dd, *J* = 287.9, 298.3 Hz, *C*). ^{19}F NMR (373 MHz, $CDCl_3$, δ): –87.6 – –87.5 (m, 1F), –83.1 (dd, *J* = 25.0, 29.8 Hz, 1F). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{20}H_{26}F_2O_3$, 352.1850; found, 352.1846.

(E)-1-(1,1-Difluoro-6-phenylhexa-1,3-dien-3-yl)-4-methoxybenzene [(*E*)-**4f**]. The reaction was conducted with 32.0 mg (0.10 mmol) of **3g** and the corresponding aryl bromide for 20 h. The product (*E*)-**4f** was obtained in 59 % yield (17.6 mg, 0.059 mmol, *E*/*Z* = 94/6) with small amount of byproducts. *E*/*Z* ratio was determined by ^{19}F NMR analysis of crude mixture. ^{1}H NMR (396 MHz, $CDCl_3$, δ): 2.50 (q, *J* = 7.8 Hz, 2H), 2.78 (t, *J* = 7.7 Hz, 2H), 3.81 (s, 3H), 4.99 (dd, *J* = 2.4, 26.1 Hz, 1H), 5.79 (t, *J* = 7.1 Hz, 1H), 6.81–6.87 (m, 2H), 7.16–7.33 (m, 7H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 31.4 (*C*H_2), 35.5 (*C*H_2), 55.2 (*C*H_3), 78.3 (dd, *J* = 16.1, 27.4 Hz, *C*H), 113.5 (*C*H), 125.9 (*C*H), 127.7 (*C*H), 128.36 (*C*H), 128.45 (*C*H), 129.2–129.4 (m, *C*), 130.6 (d, *J* = 2.8 Hz, *C*), 133.3 (*C*), 141.6 (*C*), 155.8 (dd, *J* = 290.4, 297.9 Hz, *C*), 158.9 (*C*). ^{19}F NMR (373 MHz, $CDCl_3$, δ): –85.6 (d, *J* = 29.5 Hz, 1F), –80.4 (t, *J* = 26.3 Hz, 1F). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{19}H_{18}F_2O$, 300.1326; found, 300.1325.

1-(1,1-Difluoro-4-methyl-2-phenylpenta-1,3-dien-3-yl)-4-methoxybenzene (**4g**). The reaction was conducted with 32.4 mg (0.10 mmol) of **3d** and the corresponding aryl bromide for 20 h. The product **4g** was obtained in 54% yield (16.3 mg, 0.054 mmol). ^{1}H NMR (396 MHz, $CDCl_3$, δ): 1.83 (s, 3H), 1.87 (s, 3H), 3.75 (s, 3H), 6.74–6.78 (m, 2H), 7.04–7.09 (m, 2H), 7.15–7.21 (m, 1H), 7.25–7.34 (m, 4H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 21.7 (*C*H_3), 22.1 (*C*H_3), 55.1 (*C*H_3), 95.7 (dd, *J* = 13.2, 23.6 Hz, *C*), 113.2 (*C*H), 126.9 (*C*H), 128.2 (t, *J* = 4.3 Hz, *C*H), 128.3 (*C*H), 130.3 (*C*H), 132.7 (*C*), 133.0 (t, *J* = 4.3 Hz, *C*), 135.5 (*C*), 153.2 (dd, *J* = 287.0, 299.3 Hz, *C*), 156.2 (*C*), 158.0 (*C*). ^{19}F NMR (373 MHz, $CDCl_3$, δ): –91.6 (d, *J* = 34.3 Hz, 1F), –86.2 (d, *J* = 32.1 Hz, 1F). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{19}H_{18}F_2O$, 300.1326; found, 300.1324.

1-[1,1-Difluoro-3-(4-methoxyphenyl)-4-methylpenta-1,3-dien-2-yl]naphthalene (**4h**). The reaction was conducted with 36.9 mg (0.0997 mmol) of **3f** and the corresponding aryl bromide for 6.5 h. The product **4h** was obtained in 76% yield (26.4 mg, 0.075 mmol). ^{1}H NMR (396 MHz, $CDCl_3$, δ): 1.74 (s, 3H), 2.13 (d, *J* = 2.0 Hz, 3H), 3.66 (s, 3H), 6.57–6.64 (m, 2H), 6.83–6.89 (m, 2H), 7.21–7.26 (m, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.38–7.44 (m, 2H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.74–7.79 (m, 1H), 7.81–7.87 (m, 1H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 21.9 (*C*H_3), 22.3 (d, *J* = 2.8 Hz, *C*H_3), 55.0 (*C*H_3), 93.2 (dd, *J* = 17.9, 22.7 Hz, *C*), 113.0 (*C*H), 125.0 (*C*H), 125.1 (d, *J* = 1.9 Hz, *C*H), 125.5 (*C*H), 125.9 (*C*H), 127.9 (d, *J* = 1.9 Hz, *C*H), 128.1 (*C*H), 128.3 (*C*H), 128.8 (t, *J* = 2.9 Hz, *C*), 130.4 (*C*H), 130.9 (t, *J* = 3.3 Hz, *C*), 131.6 (*C*), 132.4 (d, *J* = 1.9 Hz, *C*), 133.6 (*C*), 134.2 (*C*), 152.1 (dd, *J* = 290.8, 294.6 Hz, *C*), 157.9 (*C*). ^{19}F NMR (373 MHz, $CDCl_3$, δ): –88.5 (d, *J* = 29.8 Hz, 1F), –87.9 (d, *J* = 29.5 Hz, 1F). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{23}H_{20}F_2O$, 350.1482; found, 350.1483.

1-[1-(4,4-Dimethylcyclohexylidene)-3,3-difluoro-2-(naphthalen-1-yl)allyl]pyrene (**4i**). The reaction was conducted with 37.6 mg (0.102 mmol) of **3f** and the corresponding aryl bromide for 23 h. The product **4i** was obtained in 55% yield (24.9 mg, 0.056 mmol). ^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.54 (s, 3H), 2.40 (d, *J* = 2.4 Hz, 3H), 7.01–7.09 (m, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.22–7.35 (m, 4H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.93–7.98 (m, 3H), 8.03 (d, *J* = 9.4 Hz, 1H), 8.11 (d, *J* = 7.8 Hz, 2H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 22.1 (*C*H_3), 22.2 (d, *J* = 2.8 Hz, *C*H_3), 93.7 (t, *J* = 20.3 Hz, *C*), 124.2 (*C*H), 124.6 (*C*), 124.7 (*C*H), 124.8 (*C*H), 124.88 (*C*H), 124.95 (*C*H), 125.5 (*C*H), 125.7 (*C*H), 125.9 (*C*H), 126.9 (*C*H), 127.1 (*C*), 127.2 (*C*H), 127.3 (*C*H), 127.4 (*C*H), 128.0 (*C*H), 128.17 (*C*H), 128.20 (*C*H), 129.1 (*C*), 130.0 (*C*), 130.4 (*C*), 130.9 (*C*), 131.1 (*C*), 131.9 (*C*), 133.4 (*C*), 135.4 (*C*), 136.5 (*C*), 151.9 (t, *J* = 292.7 Hz, *C*). ^{19}F NMR (373 MHz, $CDCl_3$, δ): –89.4 (d, *J* = 31.7 Hz, 1F), –86.7– –86.4 (m, 1F). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{32}H_{22}F_2$, 444.1690; found, 444.1689.

Diels–Alder Reaction Procedure and Product Characterization

Diels Alder reaction was performed according to the reported procedure.[9c] 4-Phenyl-1,2,4-triazoline-3,5-dione (69.3 mg, 0.40 mmol) was placed in an oven-dried reaction vial. The flask was then evacuated and backfilled with nitrogen three times. Toluene (0.48 mL) and **3b** (31.0 mg, 0.10 mmol) were added to the reaction vial, and the resulting solution was stirred at room temperature for 21 h. After the reaction mixture was passed through a short silica gel column eluting with Et_2O, the crude material was purified by flash silica gel column chromatography (SiO_2, EtOAc/hexane, 0:100– 15:85). **6** was obtained in 30% yield (14.7 mg, 0.030 mmol) as a white solid. ^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.97 (s, 3H), 1.04 (s, 3H), 1.34 (s, 12H), 1.35–1.44 (m, 2H), 1.67–1.78 (m, 2H), 2.06–2.17 (m, 2H), 2.34 (dt, *J* = 4.4, 14.8 Hz, 2H), 6.28 (t, *J* = 3.7 Hz, 1H), 7.38–7.43 (m, 1H), 7.45–7.53 (m, 4H). ^{13}C{^{1}H} NMR (99 MHz, $CDCl_3$, δ): 24.7 (*C*H_3), 25.8 (*C*H_3), 28.3 (*C*H_2), 29.0 (*C*), 30.7 (*C*H_3), 34.4 (*C*H_2), 64.8 (*C*), 85.0 (*C*), 113.5 (t, *J* = 251.6 Hz, *C*), 120.9 (*C*), 126.1 (*C*H), 126.7 (t, *J* = 29.7 Hz, *C*), 128.7 (*C*H), 129.2 (*C*H), 130.5

(*C*), 150.6 (d, *J* = 25.4 Hz, *C*). The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation. ^{19}F NMR (373 MHz, $CDCl_3$, δ): –83.25– –83.20 (m, 2F). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{25}H_{32}{}^{10}BF_2N_3O_4$, 486.2490; found 486.2496.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org

Details of reaction optimizations, 2D NOESY analysis, ^{1}H, ^{13}C and ^{19}F NMR spectra of all compounds

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Notes

The authors declare no competing financial interest.

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